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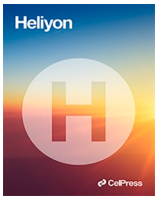

Research article

Evaluation of potentially toxic elements in soils developed on limestone and lead-zinc mine sites in parts of southeastern Nigeria

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ABSTRACT

The present study investigated the distribution of elements and potentially toxic elements (PTEs) in soil profiles in the southeastern region of Nigeria, where unrefined and primitive mining practices are common. Soil samples were collected from mine and non-mine sites in Ameka and Nkalagu and analyzed for total elemental concentration using portable X-ray fluorescence (pXRF). The results showed that the Ameka mine-affected soils were heavily polluted, while the Ameka non-mine-affected soils were moderately polluted. The Nkalagu mine and non-mine-affected soils were also moderately polluted. The potential ecological risk (PER) was high in the Ameka mine-affected site due to elevated As, Cu, and Pb levels, while the Ameka non-mine-affected site had a low PER. The enrichment factor (EF) values indicated more enrichment of PTEs in the mine-affected sites compared to the non-mine-affected sites. The geoaccumulation index (Igeo) showed moderate to extreme contamination in the Ameka mine-affected site with Cu, Zn, As, and Pb. In contrast, the Nkalagu mine-affected site had considerably lower contamination. The regression model showed that site characteristics alone were insufficient to explain elements and PTEs distribution, emphasizing the importance of considering soil properties in understanding their spatial patterns. The study highlights the higher concentrations of As, Cu, and Pb in the mine-affected sites compared to the non-mine areas and recommends remediation strategies for these elements and PTEs, especially in the vicinity of mine sites. Further laboratory analysis is recommended to understand the mobility of PTEs with depth for better remediation approaches.

1. Introduction

Soil is a crucial component of an ecosystem because much of the quality of the environment and water depends on the status of the soil's health [1]. Soil contamination originates from various organic and inorganic pollutants from anthropogenic activities such as improper agricultural management approaches, mining, and industrial activities [2–5]. These anthropogenic activities result in unfavourable environmental conditions and the degradation of agricultural fields [3,4,6], releasing large amounts of potentially toxic

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elements (PTEs). Trace and harmful elements with a weight density greater than or equal to 5 g cm^{-3} are collectively called potentially toxic elements (PTEs) [7]. Mining activities are some of the most important sources of PTEs contamination in the soil. For instance, in Central Spis, Togo, and Iraq, significant amounts of Ni and Cr have been found in soils close to mining sites [8–10]. Chen et al. [11] reported high pollution levels from Cd, Cu, Zn and As in the sites near Cu mine sites in the world, especially posing potential ecological risk. Han et al. [12] observed severe pollution in the soils of the molybdenum mines in central China, and Khafouri et al. [13] reported substantial Cd, Cu, Zn, and Pb enrichment in the soils surrounding the Ouixane mining site. Nevertheless, PTEs were tolerable in China's abandoned manganese mining region [14]. The result in Iran's Pb–Zn mining region revealed that Cd and Pb concentrations were higher than the background levels [15], while Vuong et al. [16] reported a high level of contamination in an active Pb–Zn mine in Vietnam. In Enyigba, Nigeria, Obasi and Akudinobi [17] reported severe Cd, Cu, Pb, and Zn contamination of cropland near a Pb–Zn mine site, while a gold mine in southwest Nigeria increased the accumulation of PTEs in the surrounding soil, which posed a threat to human health [18,19]. Besides that, Bahloul et al. [20] outlined that some of these PTEs are naturally occurring, but most are anthropocentric. Therefore, it is essential to control/mitigate the consequential effect of mining sites on human health.

Mining has affected the environment, including humans, crops, animals, vegetation, and surrounding water bodies resulting in erosion, loss of biodiversity, soil contamination, and ground- and surface-water contamination. Unfortunately, the situation is even worse in sub-Saharan Africa [21], where poverty has led to the proliferation of primitive and unregulated mining practices. The lack of proper equipment and safety measures exposes miners to a range of health hazards, including respiratory illnesses and injuries. It's alarming to note that many of these miners are unaware of the long-term consequences of their activities on the environment and their own well-being. The main source of contamination is mining waste and tailings released during the mining process. These materials contain PTEs and can undergo chemical reactions that further harm the environment. However, there is a lack of information about the distribution and accumulation of elements and PTEs (Al, Si, Ti, Cr, Mn Fe, Cu, Zn, As, Rb, Sr, Zr, Pb, and Th) in the soil profile of the area which acts as the primary source of elements and PTEs to water bodies, air, crops, and animals. Therefore, we hypothesized that soil properties are drivers of the distribution of elements and PTEs in both soil and sediments. Understanding the soil dynamics would aid in the explicability of elements and PTEs variability within the soil profile or across the landscape. Thus, the present study aims to (1) evaluate the distribution of elements and PTEs, in soil profile and (2) evaluate the pollution level in the soil profiles of mining sites in southeastern Nigeria. These will provide a comprehensive analysis of the soil profile to inform sustainable development practices and minimize the impact of mining activities on the environment.

2. Materials and methods

2.1. Study areas

The present study was conducted in Ameka and Nkalagu, Ebonyi state, southeastern Nigeria (Figs. 1 and 2). Ebonyi State is located at an elevation of 162 m above sea level and lies between longitudes 7°30′E to 8°30′E and latitudes 5°40′N to 6°45′N. Ameka is situated

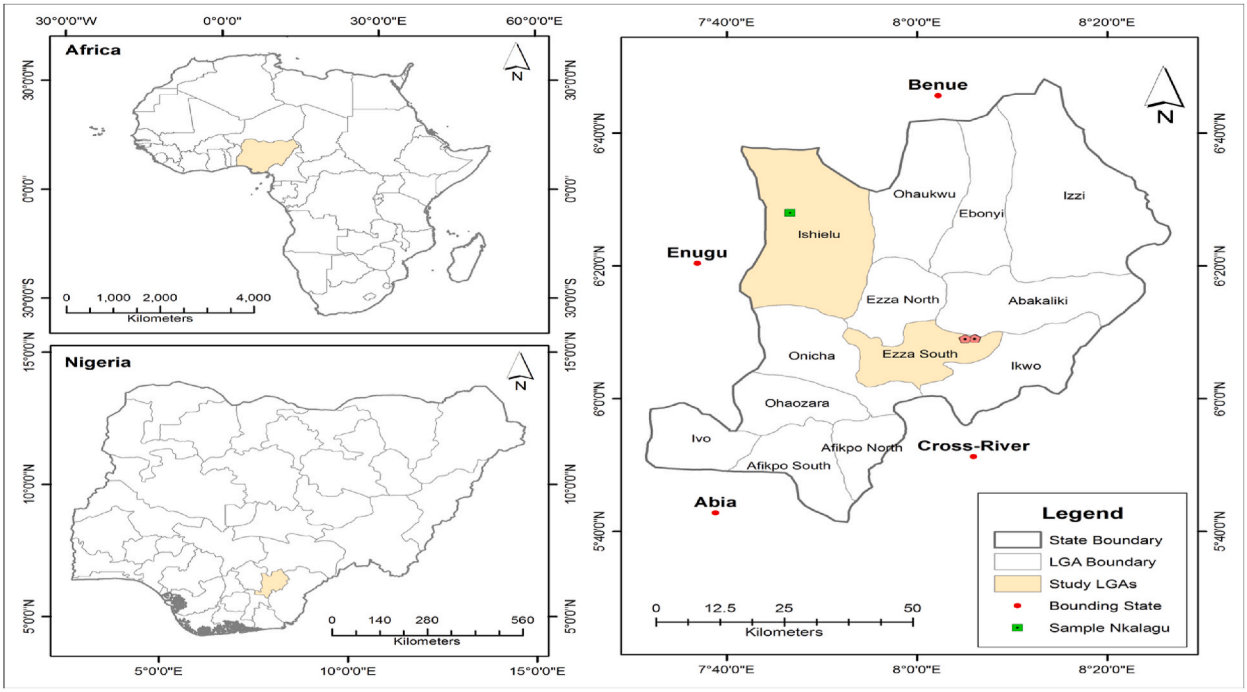

Fig. 1. Map showing the location of Ebonyi State in Nigeria, in Africa.

at longitude 8°6′37″E and latitude 6°9′46″N. In contrast, Nkalagu is located at latitude 6°29′00″N and longitude 7°46′00″E. Both are rural agrarian and mining communities with active and abandoned lead-zinc and limestone mine sites. The region experiences a mean annual rainfall range of 2000–3000 mm with a mean annual temperature of 27 °C–30° [22,23]. The area is characterized by a low rainforest and wooded/grassland-derived savannah [24].

Geologically, the sites are dominated by an Asu-river geologic group (lower cretaceous), Eze-Aku shale, and Nkporo formation. The Asu-river group is of the Albian Age (lower cretaceous) and comprises shale, sandstone, and siltstone [24]. The soil is characterized by reddish-brown and pale-coloured hydromorphic reactions, clay materials that are shallow in depth, and shale parent material [25]. The predominant crops grown in the area include paddy rice, cassava, plantain, cocoyam, maize, vegetables, and citrus and palm trees [24].

2.2. Soil sampling

The limestone and Pb–Zn mine sites and the corresponding non-mine surrounding environments were sampled in the communities of Nkalagu and Ameka, respectively. Three soil profiles were situated in mine and non-mine sites, making twelve soil profiles (Figs. 3, 4, 5 and 6)in the two study locations. The distance between the mine and the non-mine soil profile regions was above 500 m, and a stratified random sampling method was employed. Each soil profile within the mine and non-mine sites was 50 m apart. Ameka and Nkalagu mine sites are referred to as the Ameka mine affected site (MAP) and Nkalagu mine affected site (MNP), respectively. The non-mine sites are referred to as the Ameka non-mine affected site (NAP) and Nkalagu non-mine affected site (NNP), respectively. Following the soil profile description standards, the pedons were defined in situ (Tables 1, 2, 3 and 4), and 43 bulk soil samples were taken from the pedogenic horizons [26].

2.3. Laboratory analysis

Soil samples of undisturbed core were taken in reverse order (bottom to top) from the horizons to measure saturated hydraulic conductivity and bulk density.

Particle size distribution was determined by the Bouyoucos hydrometer method and soil bulk density was obtained by the undisturbed core method, while total porosity (TP) was calculated using this equation (1):

$$TP = 1 - \left(\frac{\rho_b}{\rho_s}\right) \times 100 \tag{1}$$

where TP = total porosity (%), ρ_b = bulk density (g/cm^3), ρ_S = particle density (g/cm^3).

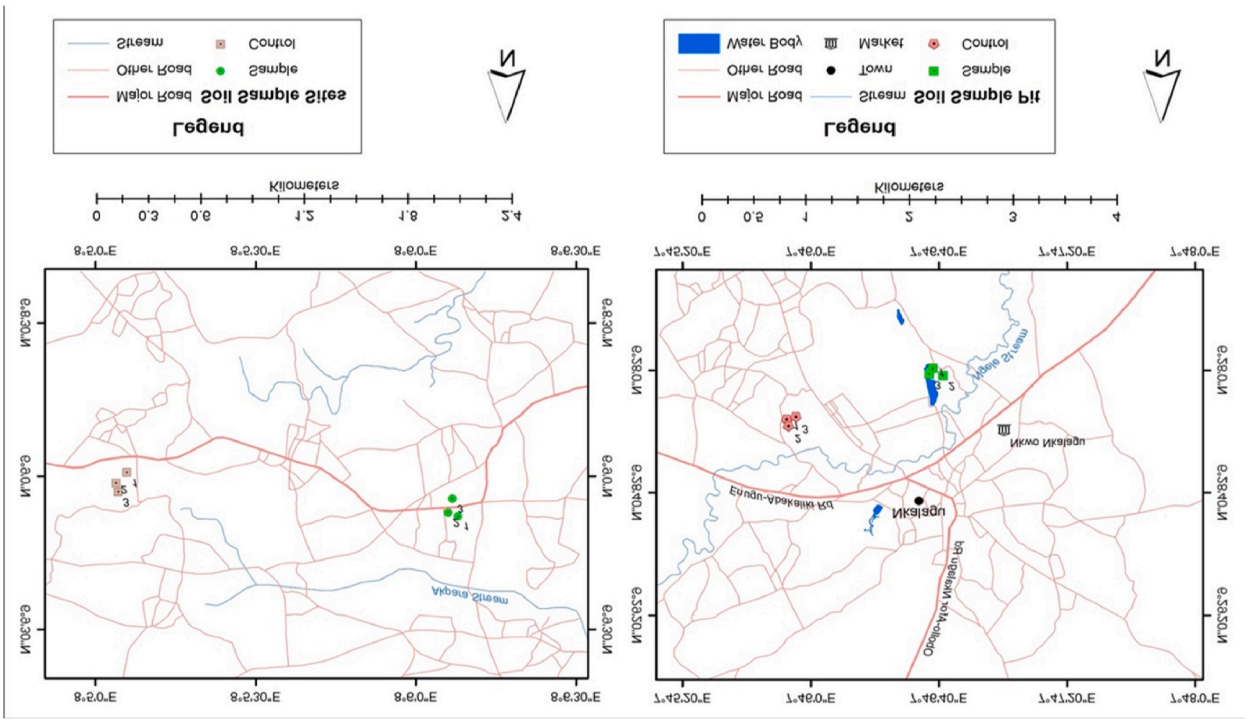

Fig. 2. Map showing the location of soil profile pit in Ameka and Nkalagu of Ebonyi State in Nigeria.

Fig. 3. Soil profile pit in Ameka mine site (MAP) of Ebonyi State, Nigeria.

Saturated hydraulic conductivity (K_s) was determined by the constant-head parameter method [27] and calculated using Darcy's equation:

$$K_s = \left(\frac{V}{At}\right)\left(\frac{L}{\Delta H}\right) \tag{2}$$

$$K_s = \left(\frac{Q}{A}\right)\left(\frac{L}{h+L}\right) \tag{3}$$

where A = cross-sectional area of the sample (cm^2), L = length of soil column (cm), H = hydraulic head difference (cm), h = height of pounded water on top of the soil column (cm), Q = flow rate = V/t (cm3/min), V = volume of percolated water collected (cm^3), t = time during which percolated water was collected (min).

Soil pH was determined in a 1:2.5 soil-to-water ratio using a digital pH meter, and soil organic carbon (SOC) was determined by the modified Walkey and Black wet digestion and oxidation method. The micro-Kjeldahl digestion, distillation, and Bray-2 processes were

Fig. 4. Soil profile pit in Ameka non-mine site (NAP) of Ebonyi State in Nigeria.

used to determine total nitrogen and available P. Exchangeable basic cations were extracted with neutral ammonium acetate (NH_4OAc), and exchangeable calcium and magnesium ions were determined in the extract by EDTA titration. A flame photometer was used to determine exchangeable K and Na ions. Exchangeable acidity was extracted using 1 *M* KCl solution and determined by titration using NaOH**.** The neutral ammonium acetate method was used to assess cation exchange capacity (CEC).

Base Saturation was calculated using the formula:

$$\%\ \text{Base saturation} = \left(\frac{summation\ of\ exchangeable\ bases}{CEC}\right) \times 100 \tag{4}$$

where *CEC* is cation exchange capacity.

2.4. Total elemental concentration analysis

10 g of air-dried soil samples were milled using a Fritsch disk mill pulverizer and then sieved to obtain a homogeneous sample. A portion of each pulverized sample was placed in the sample cup. Each soil sample was triplicated using a Delta Premium Portable X-ray fluorescence spectroscopy (pXRF) system (Olympus Innov-X, USA). A computer installed with pXRF software-scanned each soil sample for complete element concentrations following EPA guidelines [28]. Every soil sample was scanned three times for PTEs quality assurance, and the average result was used for interpretation.

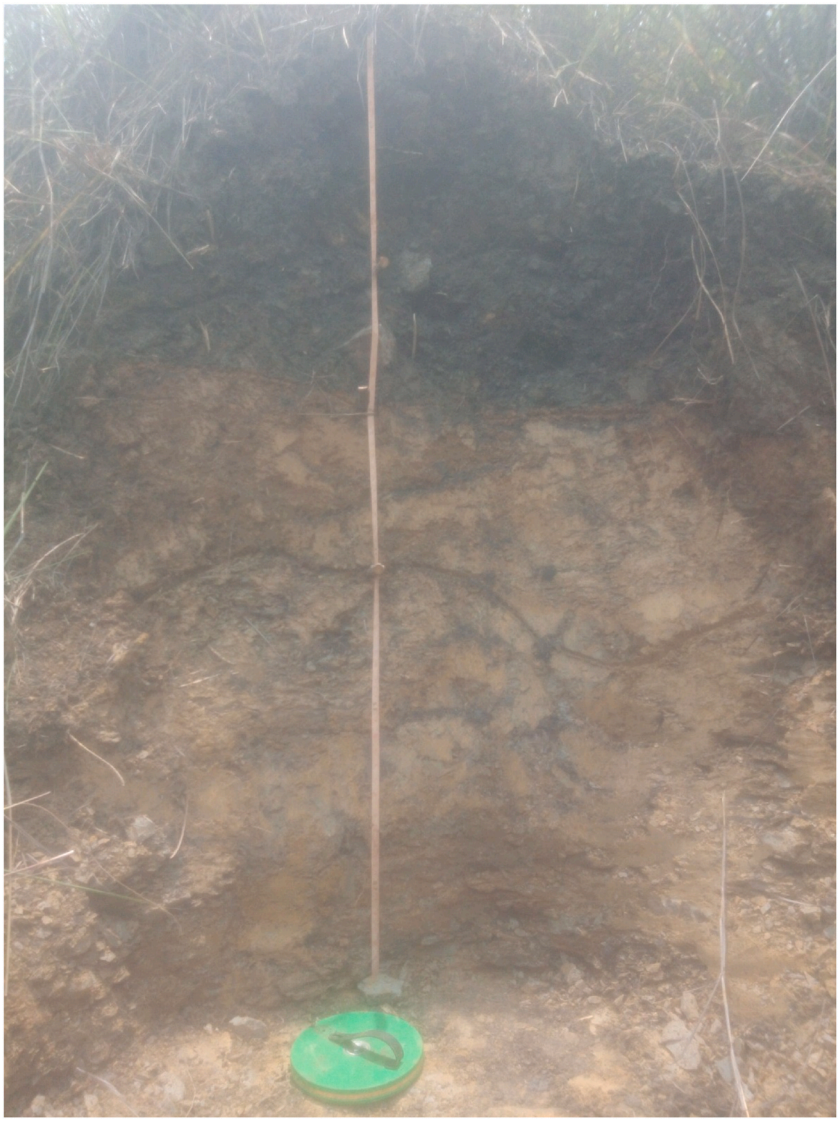

Fig. 5. Soil profile pit in Nkalagu mine site (MNP) of Ebonyi State in Nigeria.

Quality assurance and quality control (QA/QC): In the quality assurance and control process, the standard reference material for a portable device (pXRF 2711a NIST-National Institute of Standards and Technology) was used in the analysis to ensure quality compliance. The reference material is pXRF 2711a NIST-National Institute of Standards and Technology, which is an alloy material used to calibrate the equipment before measuring the soil samples and the equipment is recalibrated after every 10 soil samples are measured. The reference material was occasionally measured alongside soil samples to ensure the analysis remained accurate until completion. The detection limits of pXRF for the PTEs tested were 10 mg/kg (Cu), 5 mg/kg (Sr), 5 mg/kg (Ti), 10 mg/kg (Fe), 5 mg/kg Mn, 5 mg/kg (Zn), 5 mg/kg (As), 5 mg/kg (Pb), 10 mg/kg (Cr), 5 mg/kg (Zr), 5 mg/kg (Th), 5 mg/kg (Rb). The PTEs recovery percentages were 89.9 (Cu), 86.4 (Sr), 84.7 (Ti), 87.9 (Fe), 99.1(Mn), 81.2 (Cr), 92.5 (Zr), 100.9 (Th) 92.1(As) 85.7 (Zn) 80.4 (Pb) and 98.7 (Rb).

2.5. Environmental pollution indicators

2.5.1. Enrichment factor (EF)

Enrichment factor (EF) is applied to determine the PTEs sources (i.e., geogenic or anthropogenic). Therefore, this study used Silicon (Si) as the reference element to estimate EF values. The PTE enrichment factor was calculated using equation (5).

Fig. 6. Soil profile pit in Nkalagu non-mine site (NNP) of Ebonyi State in Nigeria.

$$EF = \left(\frac{Cm}{Csi}\right) \Big/ \left(\frac{Cref}{Si\ ref}\right) \tag{5}$$

where,

$\left(\frac{Cm}{Csi}\right)$ = ratio of metal concentration (mg kg^{-1}) in relation to Si (mg kg^{-1}) in sediment samples.

$\left(\frac{Cref}{Si\ ref}\right)$ = ratio of metal concentration (mg kg^{-1}) in relation to Si (mg kg^{-1}) in the

Antoniadis et al. [29], categorized EF contamination as EF < 1 indicates no enrichment, EF $= 1$–3 is minor enrichment, EF $= 3$–5 is moderate enrichment, EF $= 5$–10 is moderately severe enrichment, EF $= 10$–25 is severe enrichment, EF $= 25$–50 is very severe enrichment and

EF > 50 is extremely severe enrichment.

2.5.2. Contamination factor (CF)

The ratio of the metal concentration in the sample to the background value of the metal defines the contamination factor [30]. It is expressed as:

$$CF = C(metal)/C(background\ ref.) \tag{6}$$

Table 1
General site information for MAP1 (PEDON 1).

Location		Ameka (Latitude: 06.152167, Longitude: 08.102204).
Soil parent material		Undifferentiated basement complex
Geology		Basement complex
Topography		Crest
Vegetation/land use		Tropical rainforest; mining (Pb and Zn mine site)
Soil erosion hazard		Slight sheet erosion; excavated mins spoil
Drainage		Very well drained
Depth to water table		None
Depth to impenetrable layer		None
Date sampled		August 4, 2021
Horizon	Depth (cm)	Description
Ap	0–52	Dark reddish gray (5 YR 4/2) gravelly loamy sand; weak medium granular structure; slightly sticky (wet) very friable (moist); many fine and few coarse pores; many fine roots; manganese nodules; manganese; clear smooth boundary.
BA	52–99	Yellowish red (5 YR 5/6) gravelly sandy clay; weak medium sub-angular blocky structures; slightly sticky (wet) very friable (moist); few very fine pores; few fine roots; iron-Mn concretions; clear smooth boundary.
Bt	99–134	Light brown (7.5 YR 6/4) gravelly clay loam; moderate medium sub angular blocky structures; sticky (wet) firm (moist); few thin cutans on ped faces; many iron nodules; hermatite plentite; clear wavy boundary.
Crt	134–200	Dark red (10 YR 3/6) clay with many coarse prominent white (2.5y 8/1) mottles; moderate medium sub angular blocky structures; very sticky (wet) very firm (moist); common moderate cutans on ped faces; clear indication of saprolite (weathered bed rode material) or rotten rock; clear wavy boundary.

Table 2
General site information for NAP1 (PEDON 1).

Location		AMEKA (Latitude: 06.149790, Longitude: 08.084959, 59 m above sea level).
Soil parent material		Undifferentiated basement complex
Geology		Basement complex
Geomorphology		Gently sloping or undulating, 2–4 %
Topography		Mid slope
Vegetation/land use		Tropical rainforest; cassava plot; fallow and tree crops
Soil erosion hazard		None
Drainage		Poorly drained
Depth to water table		110 cm
Date sampled		August 4, 2019.
Horizon	Depth (cm)	Description
Ap	0–30	Dark reddish brown (2.5 YR 2.5/3) gravelly loamy sand; weak medium granular structures; slight sticky (wet) very friable (moist); common many medium pores; common medium roots; common Earthworms and Ants; clear wavy boundary.
BA	30–60	Dark reddish brown (5 YR 3/3) gravelly loamy sand; weak medium sub angular blocky structures; slightly sticky (wet) friable (moist); few thin clay cutans on ped faces; few common and fine pores; few very fine roots; Fe nodules; Earthworms; gradual smooth boundary.
Bt	60–110	Reddish brown (5 YR 5/4) clay loam with few medium faints red (7.5R 4/6) mottles; moderate medium sub angular blocky structures; sticky (wet) firm (moist); few moderate clay cutans on ped faces; few very fine pores; Fe nodules.

The C (metal) sample is analyzed soil's metal concentration, and the C (background ref.) is the geochemical background concentration. The background values used were the World Average Value (WAV) [31]. Based on the CF values, soil or sediment contamination is categorized into the following classes [30].

$CF < 1$ refers to the low contamination factor, $1 \leq CF < 3$ refers to the moderate contamination factor, $3 \leq CF < 6$ refers to the considerable contamination factor, and $CF \geq 6$ refers to the very high contamination factor.

2.5.3. Degree of contamination (Cdeg)

The degree of contamination was calculated using:

$$Cdeg = \sum_{i=1}^{n} CF \tag{7}$$

where CF = contamination factor, n = number of analyzed PTE. Cdeg value was rated as thus Cdeg <8 = low degree of contamination,

Table 3
General site information for MNP1 (PEDON 1).

Location		NIGERCEM (Latitude: 06.466493, Longitude: 07.777257)
Soil parent material		Limestone
Geology		Sedimentary Basin
Geomorphology		Level to nearly (0–2%)
Topography		Mid slope
Vegetation/land use		Tropical rainforest
Soil erosion hazard		Moderate gully
Drainage		Moderately well drained
Depth to water table		None encountered at 200 cm
Depth to impenetrable layer		None at 200 cm
Date sampled		July 27, 2021
Horizon	Depth (cm)	Description
Ap	0–54	Dark gray (2.5Y 4/1) loamy sand; weak medium granular structure; slightly sticky (wet) very friable (moist); many medium and coarse pores; common medium roots; few Ants and Earthworm; gradual wavy boundary.
Ab	54–90	Dark gray (10 YR 8/8) loamy sand; weak medium granular structures; slightly sticky (wet) very friable (moist); common and medium pores; fine medium roots; few Ants and Earthworm; few cobbles; abrupt smooth boundary.
Bt	90–125	Yellow (10 YR 8/8) clay loam clay with common medium faints gray (10 YR 5/1) mottles; moderate and medium sub-angular blocky structure; sticky (wet) firm (moist); few thin clay cutans on ped faces; few fine pores; few medium roots; very few mica flakes and muscovite; gradual wavy boundary.
Crt	125–200	Yellowish brown (10 YR 5/8) clay with common medium distinct gray (2.5Y 5/1) mottles; moderate coarse sub-angular blocky and platy structure; very sticky (wet) firm (moist); common moderate clay cutans on ped faces; few very fine pores; few medium roots; common mica flakes and muscovite.

Table 4
General site information for NNP1 (PEDON 1).

Location		NIGERCEM (Latitude: 06.471168, Longitude: 07.764582).
Soil parent material		limestone
Geology		Sedimentary Basin
Geomorphology		Gently sloping or undulating, 2–4 %
Topography		Mid slope
Vegetation/land use		Tropical rainforest; cassava farm (abandoned)
Soil erosion hazard		None sheet erosion
Drainage		Well drained
Depth to water table		None encountered
Depth to impenetrable layer		None at 155 cm
Date sampled		July 27, 2021
Horizon	Depth (cm)	Description
Ap	0–33	Black (5 YR 2.5/1) loamy sand; weak medium granular structure; slightly sticky (wet) very friable (moist); many medium pores; many medium roots; few Ants; few Termites; clear smooth boundary.
Bt	33–82	Pinlash gray (7.5 YR 7/2) sandy clay loam with few medium distinct reddish (7.5R 3/6) mottles; moderate medium sub angular blocky and angular blocky structures; sticky (wet) firm (moist); few thin clay/Fe cutans on ped faces; many fine pores; common and very fine roots; Fe nodules; gradual wavy boundary.
Bt2	82–125	Strong brown (7.5 YR 5/6) clay loam with few medium distinct reddish (7.5 YR 3/6) mottles; moderate medium sun angular blocky structure; sticky (wet) firm (moist); few moderate clay/Fe cutans on ped faces; Mn nodules; gradual diffuse and wavy boundary.
Crt	125–155	Red (2.5 YR 5/6) clay with common medium faints gray (7.5 YR 5/1) mottles; moderate medium angular blocky structure; sticky (wet) firm (moist); very few thin clay cutans on ped faces; Mn nodules

$8 <$ Cdeg $<16 =$ moderate degree of contamination, $16 <$ Cdeg $<32 =$ considerable degree of contamination, $32 =$ high degree of contamination [30].

2.5.4. Geoaccumulation index (Igeo)

The Geoaccumulation index assessed contamination by comparing the current levels of PTE concentrations to the background level

of the area. Considering the natural background value, it is used to understand PTE's present environmental and pollution status [32]. The index calculates contamination while comparing preindustrial and recent metal concentrations [33]. The background values used were WAV [31]. The Igeo is calculated using this equation:

$$\text{Igeo} = Log\ 2\left(C_{metal}/1.5 * C_{background\ ref.}\right) \tag{8}$$

C (metal) represents the concentration of an individual PTE in the sample, C (background ref.) is the background reference concentration of PTE [31], and 1.5 is the constant compensating for possible variations due to the lithogenic effects. The estimated result can be interpreted using the precise scale [13] presented as thus: Class 0 = Igeo ≤0 (practically uncontaminated), Class 1 = 0 <Igeo ≤1 (uncontaminated to moderately contaminated), Class 2 = 1≤ Igeo <2 (moderately contaminated), Class 3 = 2 ≤ Igeo <3 (moderately to heavily contaminated), Class 4 = 3 ≤ Igeo <4 (heavily contaminated), Class 5 = 4≤ Igeo <5 (heavily to extremely contaminated), Class 6 = Igeo >5 (extremely contaminated).

2.5.5. Pollution load index (PLI)

The pollution load index (PLI) was estimated as the product of the individual CF values of all studied potentially toxic elements, as per Rinklebe et al. [34] and Shaheen et al. [35]:

$$\text{PLI} = (CF_1 \text{ x } CF_2 \text{ x } CF_3 \text{ x } \ldots \text{ x } CF_n)^{1/n} \tag{9}$$

where CF is the contamination factor, CFs, 1, CFs, 2, CFs, n are the contamination factors of elements 1, 2, …, n under consideration. PLI >1 indicates substantial PTE soil contamination of the area under study. No pollution (PLI,< 1), moderate pollution (1 < PLI, <2), heavy pollution (2 < PLI <3), and extremely heavy pollution (PLI, ≥ 3).

2.5.6. Ecological risk factor (Er)

Er was applied to estimate the ecological risk for individual pollutants based on toxicity response [30], which can be calculated as:

$$ERi = Tr * CFi \tag{10}$$

where Tr is the toxicity response of each metal, and CF is the contamination factor of the corresponding metal. Seven selected metals (Pb, Cu, Zn, Fe, Mn, Cr, and As) have the following values of toxic response: Zn = Fe = Mn = 1; Pb = Cu = 5; Cr = 2; As = 10 [30,32, 36–38]. Er rates the single index of ecological risk factors as < 40 = low, 40–80 = Moderate, 80–160 = considerable, 160–320 = high and >320 = very high potential ecological risk.

2.5.7. Potential ecological risk index (RI)

RI was applied to evaluate the magnitude of environmental sensitivity led by toxic metals in the soil environment [39]. RI can be calculated [30] as:

$$RI = \sum_{i=1}^{n=7} ERi \tag{11}$$

RI was calculated for seven (n) metals Classification: <150 = low, 150–300 = moderate, 300–600 = considerable, >600 = very high potential ecological risk.

2.6. Data analysis

Data obtained from soil profile samples were subjected to summary statistics (mean, minimum, maximum, and standard deviation) using SPSS Statistic 21 software (IBM, Armonk, NY, USA). Line graphs were also created to display concentrations of measured elements and PTEs values within the soil profile. Pollution indices were integrated to assess the soil's PTE pollution level and discussed according to summarized soil master horizons (A, B, C) as in the study of Ji et al. [32] and Zhang et al. [40]. Pearson correlation and linear regression were performed with R software.

3. Results and discussion

3.1. Correlation of potentially toxic elements and soil properties in the studied soils

The correlation matrix (Fig. 9) indicated strong positive correlations between several elements and potentially toxic elements (PTEs): Zn and Cr, Pb and Fe, Cu and clay, Mn and sand, Th and Ti, Ti and clay, and Zn and Fe. Moreover, a stronger positive correlation was observed between Mn and Cr, Pb and As, Pb and Cu, As and Cu, Rb and Sr, Rb and Al, and Al and clay.

In contrast, strong negative correlations were found between Pb and pH, Sr and Si, Si and Rb, Fe and pH, Cu and pH, and As and pH. Additionally, a strong negative correlation was observed between As and silt.

Furthermore, stronger correlations were identified between Zr and Rb, sand and clay, and Zr and Al. Elements and PTEs that displayed strong positive correlations with each other are likely to have originated from the same or closely related sources. Conversely, elements with negative or weak correlations are more likely to have different origins [41].

Additionally, Mensah et al. [42] reported that the negative relationships between elements and soil properties may be attributed to mutual influences exerted by each other.

3.2. Elements and potential toxic element (PTEs) concentrations in the studied soils

The concentrations of studied elements, including PTEs from all sites, are presented in Fig. 7 and further discussed below: The Ameka mine-affected sites (MAP), Ameka non-mine-affected sites (NAP), Nkalagu mine-affected (MNP) and non-mine-affected sites (NNP).

The concentration of PTEs and elements such as *Aluminium (Al)* in soils could be influenced by various factors, including soil depth, anthropogenic activities, regional and background concentrations, and previous research. In the study concentration of Al vary with soil depth, and organic carbon may also exhibit similar patterns. The higher concentration of Al in the mine-affected sites compared to the non-mine-affected sites could be attributed to the mobilization and deposition of Al from mine spoil. Anthropogenic activities, such as mining, can result in the disturbance of soils, leading to changes in organic carbon concentration and distribution, as well as the release and redistribution of Al in the environment. The concentration of Al observed in the study was reported to exceed the reference background concentration, indicating that the mine-affected soils had elevated levels of Al. This is consistent with previous studies that

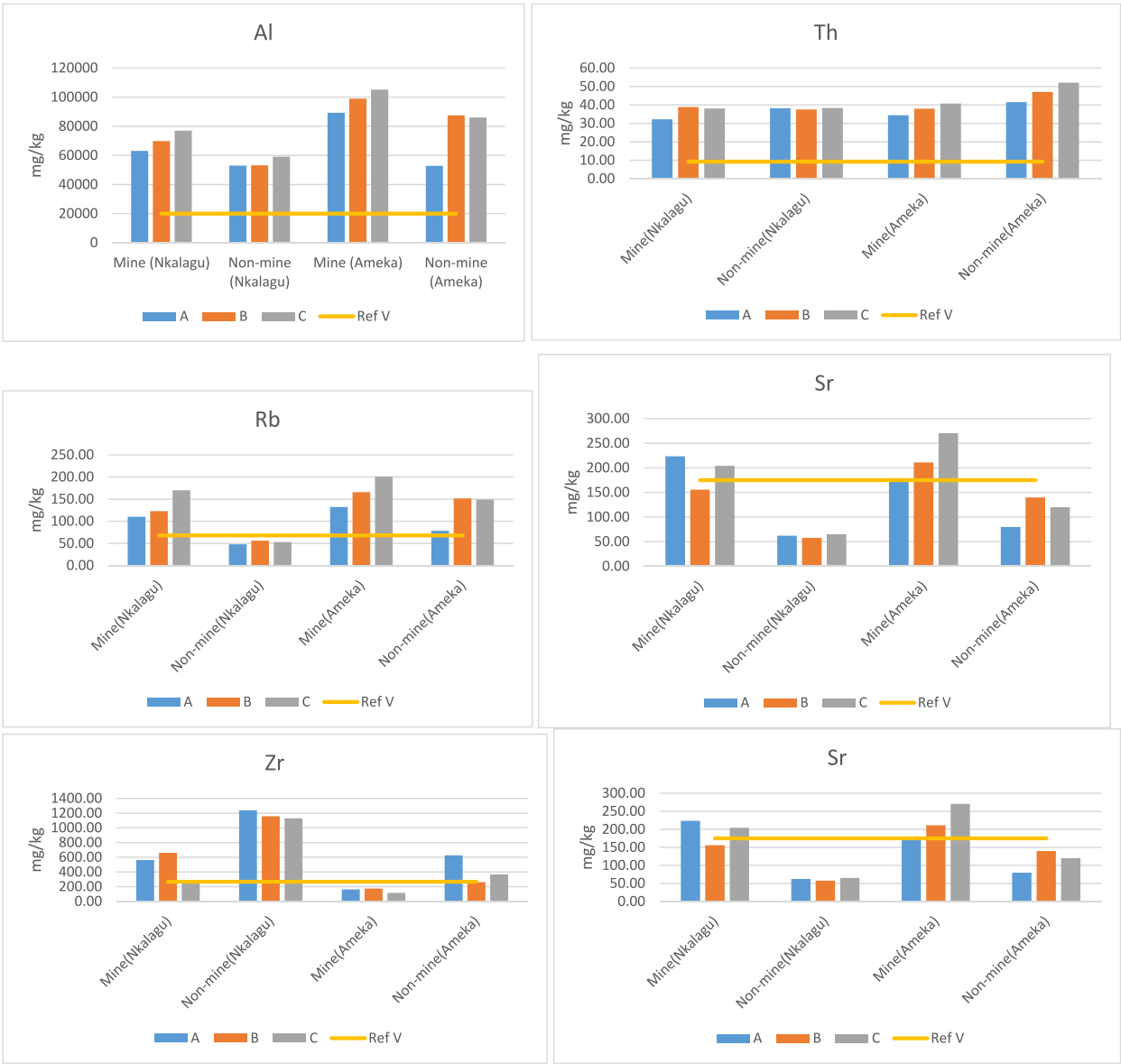

Fig. 7. Absolute potential toxic elements (mg/kg) concentrations of the studied soil (A,B, C = horizons and Ref V=Reference value).

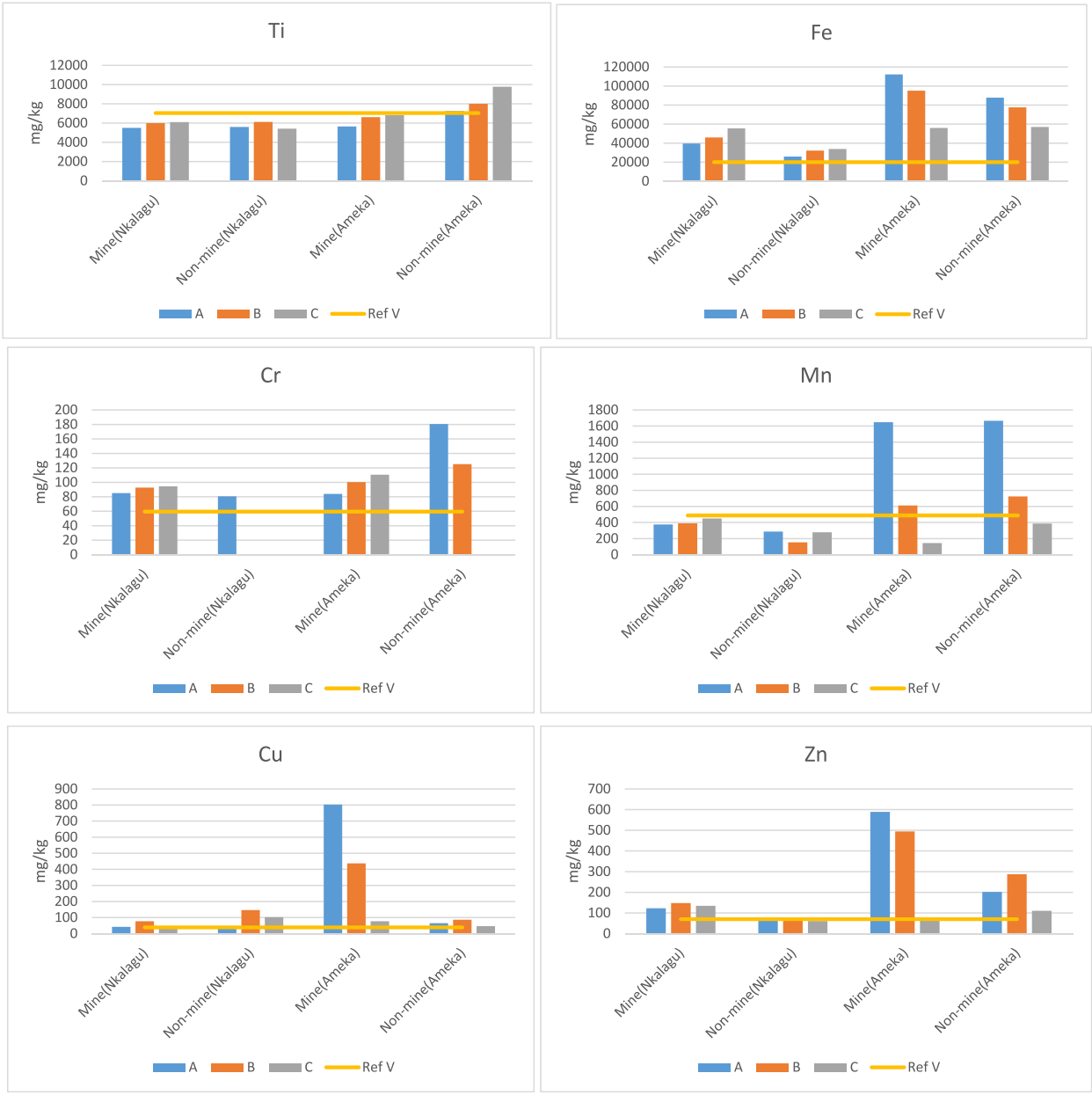

Fig. 7. (*continued*).

reported high concentrations of Al in tropical soils. Regional and background concentrations of Al can vary depending on geological and environmental factors, and these can influence the relationship between concentration of Al and organic carbon in soils. Nogueirol et al. [43] and Mensah et al. [42] documented higher concentrations of Al in mine-affected soils compared to natural forest or non-mine-affected soils. This suggests that similar factors in different studies and locations may influence the relationship between concentration of Al and organic carbon, indicating a consistent pattern. The total *rubidium (Rb)* concentration exceeded the world soil average value of 68 mg/kg [31] in all studied sites except in NNP. The higher concentration of Rb in the mine than in the non-mine affected sites of the two study locations can be associated with the mining activities. This can also be influenced by the concentration of Al in the soil, as it correlated positively (Figs. 1S–4S in the supplementary list) with Al in all study locations. The concentration of *thorium (Th)* had a positive correlation with Rb and a negative correlation with organic carbon in all study locations (Figs. 1S–4S in the supplementary list). This means that Th may be lower in soils with high carbon concentrations and higher in soils with low carbon concentrations. *Strontium (Sr)* concentration was generally higher in the mine sites than in the non-mine of the two studied locations. Strontium exceeded the world soil average value of 175 mg/kg [31] in the A, C, and A, B, C of MNP and MAP, respectively, and was below the reference value in the other studied sites' horizons. Strontium was also found to correlate (Figs. 1S–4S in the supplementary

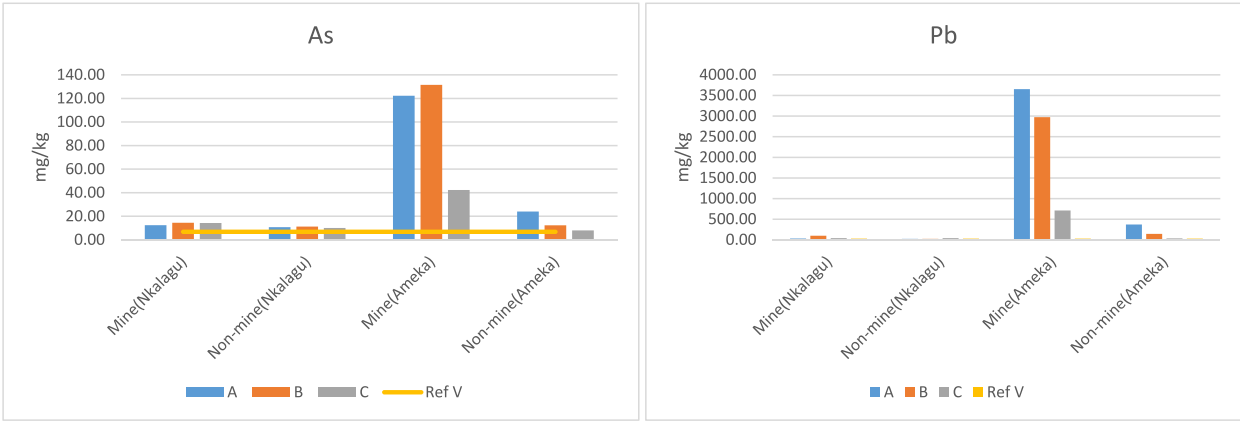

Fig. 7. (*continued*).

list) positively with Al in all study locations. *Zirconium (Zr)* in MAP and MNP horizons was lower than their respective NAP and NNP horizons. The world soil average value of Zr is 267 mg/kg [31], which was exceeded in MNP and NNP, and NAP A and C horizons. Aluminium may influence the Zr accumulation in the soils of the mine, and the non-mine affected sites of the two-study locations. Zirconium correlated (Figs. 1S–4S in the supplementary list) negatively with Al in all study sites.

Silicon (Si) exhibited the highest total concentration among the elements and potentially toxic elements (PTEs) investigated in Ameka and Nkalagu soils. Findings suggest potential differences in Si accumulation between mine-affected and non-mine-affected soils. Notably, all studied sites horizons, except the A and B horizons of NNP and the A horizon of NAP, were reported to have Si concentrations below 270,000 mg/kg by Taylor and Mclennan [44]. Additionally, Si exhibited a negative correlation (Figs. 1S and 3S in the supplementary list) with Fe in the two mine-affected sites (MAP and MNP), indicating a potential interaction between Si and Fe in these soils. The deposition of Fe may influence the accumulation of Si in mine soils, suggesting that Fe could play a role in Si dynamics in these environments. It is important to note that the relationship between Si concentration and soil organic carbon is complex and can be influenced by various factors such as soil type, land use, and management practices. Titanium *(Ti)* yielded a positive correlation (Fig. 9) with soil organic carbon, indicating that higher concentrations of Ti may be associated with higher organic carbon concentrations in soils [45]. This could be attributed to Ti common association with clay minerals, which can contribute to the stabilization of organic matter in soils by forming complexes with organic compounds and protecting them from decomposition. Titanium also correlated negatively with Cu in the mine sites of the two study locations (Figs. 1S and 3S in the supplementary list). This may be attributed to the higher concentration of Ti in the non-mine than in the mine-affected soil. The total Ti concentration variation between mine and non-mine sites may be due to the degree of weathering in each site, as Ti is an indicator of weathering condition [46]. All site horizons (except the NAP horizons of Ameka) exceeded the world soil average value of 7038 mg/kg, as Kabata-Pendias [31] reported. The concentration of iron Fe in all study sites exceeded the reference background value of 20,000 mg/kg [35,42]. The Fe in horizons A and B of the mine sites may be associated with mobilization and deposition. This is supported by the studies of Bansah and Addo [47], Mensah et al. [48], and Mensah et al. [42], respectively.

The total *chromium (Cr)* concentration in all studied sites' horizons exceeded the world soil average value of 59.50 mg/kg [31], and the high concentration of Cr recorded in MNP and NNP may be associated with the accumulation of chromium during mining activities. The *manganese (Mn)* total concentration in Ameka A and B horizons (except the C horizons of MAP, NAP, and entire horizons in MNP and NNP) exceeded the world soil average value of 488 mg/kg [31]. The higher concentration of Mn recorded in the MNP than in the NNP may be associated with the accumulation of Manganese during mining activities. The *copper (Cu)* concentration in all study sites exceeded the world soil average value of 38.9 mg/kg [31] except for the C horizon of MNP and A horizon of NNP. This Cu concentration variation may be attributed to anthropogenic sources [49]. The higher deposition of Cu in the surface horizons at MAP and MNP than in NAP and MNP sites of the two study locations, as in the study of Demkova et al. [8] in a mining area of central Spis, could be attributed to these anthropogenic mining operations. The *zinc (Zn)* concentration in the two studied locations exceeded the world soil average value of 70 mg/kg [31] except B and C horizons of NNP and the C horizon of MAP. The higher concentration of Zn in the A and B horizons of the two study mine-affected sites than in their non-mine-affected sites could be linked to anthropogenic mining activities. This concentration has been reported in abandoned lead-zinc mine sites in Morocco [50], soils of the royal salt mining company in Nigeria [51], the soil of an industrial mining area in Greece [52] and the soil of an artisanal mining area in Ghana [42].

The total *arsenic (As)* concentration in all studied sites exceeded the world soil average value of 6.83 mg/kg [31]. This indicates mining activities, and the high concentration of arsenic in the surrounding mine may be associated with transport, mobilization, and accumulation from the contaminated tailings. Similar observations were reported in Zambia and Ghana by Chileshe et al. [53] and Mensah et al. [48], and Mensah et al. [42], respectively. The high concentration of *lead (Pb)* in MAP and NAP reflects the mined Pb and indicates the strong influence of the mineral on the overlying soils. This could threaten consumers of agricultural produce in the area, as the metal may be bioaccumulated. In high concentrations, Pb could lead to the breakdown of the central nervous system and other vital human organs, such as the liver and kidney, with children having been reported to be at high risk [54]. In all the studied soils, Pb

exceeded the world soil average value of 27 mg/kg [31] except in NNP. The higher lead concentration in MAP and MNP can be traced to mining activities, which lead to the deposition of mine waste on the soil. A similar observation was reported by Uchendu et al. [51] in Nigeria, Esshaimi et al. [50] in Morocco, Leopld et al. [55] in Cameroon, and Wahsha et al. [56] in Italy. In a related study in Ghana, Essandoh et al. [57] attributed the production of salty acid leachate that contains trace elements to an increased level of potentially toxic elements in the soil. Cadmium, Cobalt, and Nickel were below the detection limit. Hence were below the world soil average value (0.41, 11.3, and 29 for Cd, Co, and Ni, respectively [31].

3.3. Contamination factor, degree of contamination and pollution load index of the studied soils

Table 5S in the supplementary material provides an analysis of the contamination factor (CF) and reveals that Cu, Zn, As, and Pb have very high contamination in the MAP and moderate to considerable contamination in MNP. Previous studies by Mensah et al. [48]; Mensah et al. [42] in Ghana; Chileshe et al. [53] in Zambia; Antoniadis et al. [58] in Greece and Shaheen et al. [35] in Egypt have reported that these metals are associated with industrial mine waste.

The degree of contamination (Cdeg) in Fig. 8 shows the total CF values of metals for each sample. MAP and NAP showed a high to considerable degree of contamination, while NNP and MNP indicated a considerable level of contamination. Studies by Chileshe et al. [53] and Demková et al. [8] also recorded high contamination in soil surrounding copper and mercury mines. The contamination in the MNP may be related to low activities in the mine sites at the time of sampling or to the limestone lithology, which has been reported to influence the concentration of potentially toxic elements [59]. Pedziwiatr et al. [60] and Xu et al. [61] have also reported evidence of lithologic source effects on PTE concentration.

To calculate the pollution load on each sample site, the pollution load index (PLI) is used. The PLI (Fig. 8) in this study shows extremely heavy pollution in the MAP, whereas the NAP indicated heavy to moderate pollution. Nkalagu generally indicated moderate pollution levels in the MNP and NNP. The PLI is considered the best way to determine the pollution load on a specific sample site [32, 62].

3.4. Ecological risk and potential ecological risk (PER) of Cr, Mn, Fe, Cu, Zn, As, and Pb of the studied soils

Table 6S in the supplementary material indicates that the ecological risk (Er) of the seven potential toxic elements varied. Upon individual element assessment, it was found that Cr, Mn, and Fe generally pose a low ecological risk in both the MAP and NAP, as well as the MNP and NNP. Cu, on the other hand, poses a moderate to considerable ecological risk (Er) in the MAP, but a low Er in the NAP, MNP, and NNP. Zn poses low Er in both mine and non-mine affected sites in the Ameka and Nkalagu locations. Arsenic also poses low Er in NAP, MNP, and NNP except MAP where it poses high to moderate Er. Lead (Pb), poses very high to considerable Er in the MAP, but only a moderate to low Er in the NAP. The Nkalagu study showed that Pb poses low Er in both MNP and NNP horizons.

Looking at the potential ecological risk (PER) (Fig. 8), Cu, As, and Pb are likely to pose more risk in the Ameka mine surrounding ecological environment due to their high Er recorded in the soil's surface horizons with exposure to the ecosystem. The study sites showed that the MAP had a very high to moderate PER, which was mainly due to As, Cu, and Pb. In contrast, the NAP had a low PER, while the MNP and NNP had low PER overall. Therefore, it is crucial to pay attention to the remediation of As, Cu, and Pb in these sites, particularly in the Ameka mine surrounding, to avoid posing a serious hazard to human health and agricultural productivity.

3.5. Enrichment factor (EF) and geo-accumulation index (1geo) of the studied soils

The Enrichment Factor (EF) is an index used to determine the source of Potentially Toxic Elements (PTE) found in soil. An EF of less than 1.5 indicates that the PTE is entirely from natural or geogenic crustal material, while an EF greater than 1.5 suggests an anthropogenic source. In this study, EF was estimated, assuming that silicon is inert and primarily geogenic, with no significant anthropogenic source [63,64]. Silicon was used as a normalizer in sediment and soils contaminated with PTE [41], as it is highly stable, associated with clay minerals, and unaffected by environmental factors such as reduction/oxidation, adsorption/desorption, and other diagenetic processes [63,64].

The results (Table 7S in the supplementary material) of the EF index showed that the surface horizons of Ameka mine-affected soils had very severe to severe enrichment of Al, Fe, Cu, Zn, As, Pb, and Th, while Nkalagu showed moderate to non-significant enrichment, indicating more enrichment in the mine-affected soils. The higher range of enrichment of these PTEs in the mine-affected soils may be associated with lead-zinc and limestone mining activities. Artisanal gold mining in Ghana [42] and Ivory Coast [65] increased arsenic enrichment, indicating extremely severe enrichment in the former than the non-mining site.

Furthermore, the 1geo values (Table 8S in supplementary material) obtained from the soils showed that Cu, Zn, As, and Pb in MAP indicated extreme to moderate contamination with these PTEs. MNP 1geo values ranged from uncontaminated to moderately to no significant contamination. These elements were all higher in the mine-affected soils than in the non-mine-affected soils.

3.6. Linear regression model with the site (mine and unmined) and soil properties as a predictor

The findings of the study suggest that site characteristics alone are insufficient to explain the distribution of potentially toxic elements (PTEs) in both mined and non-mined areas. As shown in Table 5, the first linear regression model examined the relationship between PTEs and the site as a factor. However, the adjusted R-squared (R^2) values were less than 0.5 for all the studied PTEs, except for Si, which had an R^2 value of 0.5. An R^2 value lower than 0.5 indicates a poor model with limited capacity to explain the distribution

Fig. 8. Mean soil pollution load index, degree of contamination and potential ecological risk index for PTE in the studied soil.

of PTEs. This suggests that factors other than site characteristics play a significant role in influencing the distribution patterns of PTEs. The study cites Li et al. [66] to support that an R^2 value below 0.5 signifies a poor model with minimal explanatory power.

To further investigate the relationship between PTEs and their distribution, a second linear regression model was conducted, integrating both site characteristics (mined and non-mined) and soil properties. Table 6 presents the results of this model. The findings indicate that when soil properties such as pH, organic carbon (OC), horizon depth, clay, and cation exchange capacity (CEC) were added to the model, the prediction of Al, Rb, and Zr significantly improved. These elements showed relatively high R^2 values ranging from 0.50 to 0.70.

This suggests that the distribution of Al, Rb, and Zr can be moderately explained by considering both site characteristics and soil properties. Conversely, the performance of Si dropped from 0.50 to 0.43 when soil properties were taken into account, implying that soil properties might have a greater influence on the distribution of Si. However, for elements such as Cu, Cr, Mn, Fe, As, Sr, and Th, the proposed model yielded lower R^2 values, all below 0.5. This indicates that the model for these PTEs was inadequate in accurately explaining their distribution in both polluted and non-polluted areas.

Overall, the significant variables that consistently emerged in all the models were site, pH, CEC, and clay, highlighting their importance in understanding the distribution patterns of PTEs. These findings suggest that a comprehensive understanding of PTE distribution requires the consideration of both site characteristics and specific soil properties rather than relying solely on on-site factors.

4. Conclusion

MAP and NAP showed a high to a considerable degree of contamination, while NNP and MNP indicated a considerable level of contamination. The pollution load index showed extremely heavy pollution in the MAP, whereas the NAP indicated heavy to moderate pollution. Nkalagu generally indicated moderate pollution levels in the MNP and NNP. The potential ecological risk estimated for study sites showed that the MAP had very high to moderate PER, influenced by As, Cu, and Pb. In contrast, NAP had a low PER. MNP and NNP generally had low PER. This shows that more attention should be paid to the As, Cu, and Pb remediation in these sites, especially at the Ameka mine surroundings, as this might pose a serious hazard to human health and agricultural productivity. The EF value of Al, Fe, Cu, Zn, As, Pb, and Th in surface horizons of the Ameka mine affected site range from very severe to severe, while that of Nkalagu shows moderate, minor to non-significant enrichment, showing more enrichment in the mine than the non-mine affected sites in the two study locations. The Igeo value of Cu, Zn, As, and Pb in MAP indicated extremely moderate contamination with these PTEs. Nkalagu MNP ranges from uncontaminated to moderately to no significant contamination. These elements' contamination levels were

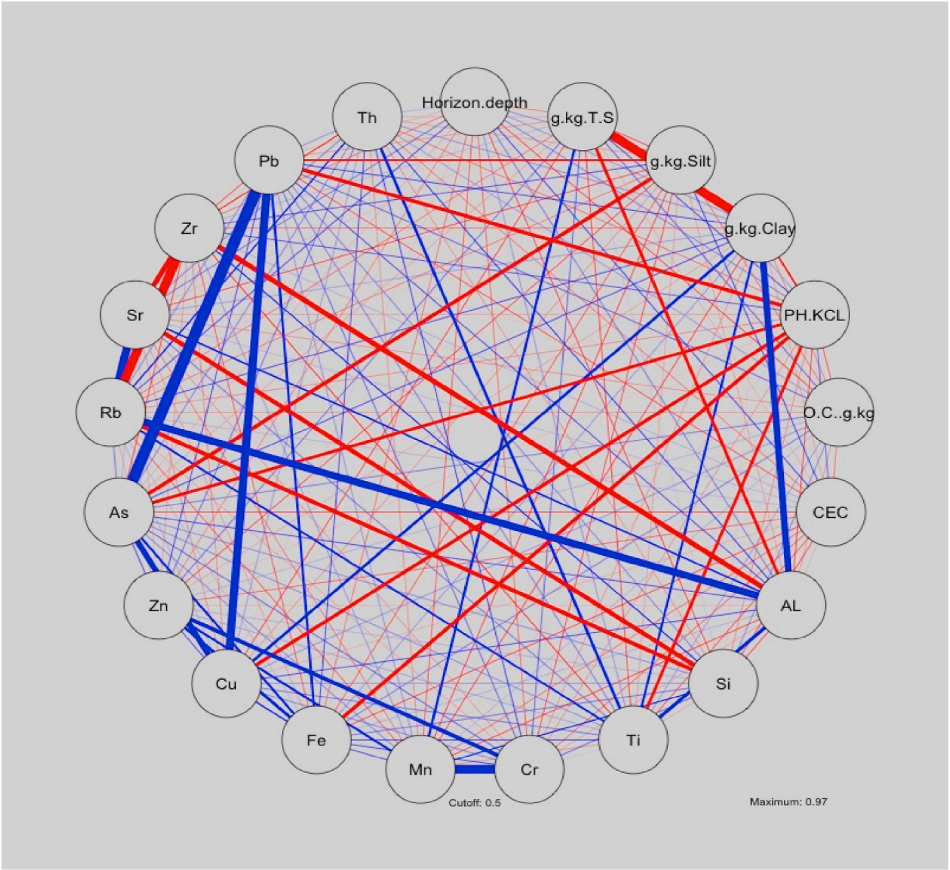

Fig. 9. Correlation of potentially toxic elements and soil properties in the studied soils.

Table 5
Linear regression model with the site, which composes of mine and unmined.

PTES with Site	Adjusted R^2	p-value (<0.05)
Al ~ Site	0.23	0.00
Si ~ Site	0.50	2.91E-07
Ti ~ Site	0.00	0.32
Cr ~ Site	0.15	0.06
Mn~ Site	0.02	0.82
Fe ~ Site	0.06	0.08
Cu ~ Site	0.06	0.06
Zn~ Site	0.04	0.11
As ~ Site	0.05	0.10
Rb ~ Site	0.30	9.56E-05
Sr ~ Site	0.48	1.54E-07
Zr ~ Site	0.31	5.54E-05
Pb ~ Site	0.05	0.1007
Th ~ Site	0.10	2.35E-02

higher in the mine than in the non-mine affected sites. Si and Ti Igeo values showed no significant contamination in all the study locations. The correlation analysis revealed strong positive correlations between various elements and potentially toxic elements (PTEs), suggesting a common source of origin.

Conversely, strong negative correlations were observed between certain elements and soil properties, indicating different origins. The first linear regression model using the site as a factor showed poor explanatory power ($R^2 < 0.5$) for most PTEs, except Si. The second model incorporating soil properties significantly improved the prediction of Al, Rb, and Zr ($R^2 = 0.50$ to 0.70), while Si's performance dropped. However, the model for Cu, Cr, Mn, Fe, As, Sr, and Th had inadequate explanatory power ($R^2 < 0.5$) in both polluted and non-polluted areas. Overall, site characteristics alone were insufficient to explain PTE distribution, emphasizing the importance of considering soil properties in understanding their spatial patterns. Further research is necessary to better understand the

Table 6
Linear regression model with the site, which compose of mine and unmined and soil properties as predictors.

PTEs with site and soil properties	Adjusted R^2	p-value (<0.05)	Significant variables
Al ~ Site + pH.KCL + O.C. + Horizon. depth + clay + CEC	0.68	6.52E-08	Site, pH.KCL, Clay,
Si ~ Site + pH.KCL + O.C. + Horizon. depth + Clay + CEC	0.46	0.00	site
Ti ~ Site + pH.KCL + O.C. + Horizon. depth + Clay + CEC	0.31	0.01	Site, pH.KCL, CEC
Cr ~ Site + pH.KCL + O.C. + Horizon.depth + Clay + CEC	0.03	0.52	
Mn~ Site + pH.KCL + O.C.+ Horizon.depth + Clay + CEC	0.09	0.17	
Fe ~ Site + pH.KCL + O.C. + Horizon.depth + Clay + CEC	0.43	0.00	pH.KCL
Cu ~ Site + pH.KCL + O.C. + Horizon.depth + Clay + CEC	0.19	0.03	Site
Zn~ Site + pH.KCL + O.C.+ Horizon.depth + Clay + CEC	0.22	0.03	Site, CEC
As ~ Site + pH.KCL + O.C.+ Horizon.depth + Clay + CEC	0.11	0.14	
Rb ~ Site + pH.KCL + O.C. + Horizon.depth + Clay + CEC	0.54	3.63E-06	Site, pH.KCL
Sr ~ Site + pH.KCL + O.C.+ Horizon.depth + Clay + CEC	0.53	6.04E-06	Site
Zr ~ Site + pH.KCL + O.C. + Horizon. depth + Clay + CEC	0.63	1.06E-07	
Pb ~ Site + pH.KCL + O.C. + Horizon. depth + Clay + CEC	0.15	0.08	Site, pH.KCL
Th ~ Site + pH.KCL + O.C. + Horizon.depth + Clay + CEC	0.19	2.83E-02	Site

mechanisms and dynamics of Si in relation to soil organic carbon in different ecosystems and under varying environmental conditions.

In conclusion**,** the study recognizes the need for an extensive and more intensive study to understand the mobility of these potentially toxic elements. This will give more insight into the remediation experiment and the remediation strategies that should be adopted for each mine surrounding. Further study may explore the PTE's speciation and bioavailability in topsoil and soil profiles.

Data availability statement

Data included in article/supplementary material/referenced in article. Other data will be made available upon reasonable request by the first author.

Ethics statement

Do not apply.

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CRediT authorship contribution statement

Egondu Charles Umeobi: Writing – review & editing, Writing – original draft, Visualization, Validation, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Chukwuebuka Vincent Azuka:** Validation, Supervision, Conceptualization. **Kokei Ikpi Ofem:** Writing – review & editing, Resources, Methodology, Investigation. **Kingsley John:** Writing – review & editing, Writing – original draft, Validation, Formal analysis, Data curation. **Karel Nemeček:** Resources, Methodology, Investigation, Formal analysis. **Chika Mike Jidere:** Validation, Resources, Conceptualization. **Peter Ikemefuna Ezeaku:** Validation, Supervision, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2024.e27503.

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